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Synthesis and Structural Characterization of 2-Benzylidenebenzofuran-3-(2*H*)-Ones

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*Novel aurone derivatives e.g. 2-(2-(3-methylbut-2-enyloxy)benzylidene)benzofuran-3(2*H*)-one (3a), 2-(2-(allyloxy)benzylidene)-7-methoxybenzofuran-3(2*H*)-one (3b), and 2-(5-bromo-2-(3-methylbut-2-enyloxy)benzylidene)-6-hydroxybenzofuran-3(2*H*)-one (3c) were synthesized. All these compounds were characterized by IR, ¹H and ¹³C NMR, and Mass spectroscopy. Finally, the crystal structures were solved by single crystal X-ray diffraction data and the structures were analyzed in terms of supramolecular interactions.*

[Supplementary materials are available for this article. Go to the publisher's online edition of Molecular Crystals and Liquid Crystals for the following free supplemental resource(s): supplemental figures 1–12; Spectral data (IR, NMR, MS, and HRMS) of the compounds 3a, 3b and 3c are available in the supporting information in .pdf format. Crystallographic information files (.cif) of compounds 3a, 3b, and 3c are available in the electronic format.]

Keywords Aurones; conformational isomers; hydrogen bonding; hydroxybenzofuran-3(2*H*)-one; single crystal X-ray diffraction; spectroscopic characterization; supramolecular synthons

Introduction

Naturally occurring aurones (or 2-benzylidenebenzofuran-3(2*H*)-ones) that belong to a type of flavonoid class possess a chalcone-like moiety part of which is closed into a 5-membered ring through an oxygen atom, and an intact exocyclic double bond with restricted rotations. These are biosynthesized from chalcones in the presence of a key enzyme called aureusidin synthase or obtained through the biosynthesis of other flavonoids [1]. These compounds exhibit a wide variety of biological activities, e.g., anticancer, antifeedant, antiparasitic, antimalarial, antihistamine, and antifungal activities [2–7]. They are also known as inhibitors of tyrosinase, iodothyronine-deiodinase, acetylcholinesterase, and as

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antioxidants [8–11]. There have been reports that some of these substances were synthesized as fluorescent probes [12–14]. The interesting biological activities and structural feature of the aurones have stimulated many studies on their synthesis.

These compounds are usually prepared by three main methods, e.g., condensation between benzofuranones and benzaldehydes, oxidative cyclization of 2-hydroxy chalcones, or catalyzed cyclization of *o*-(1-hydroxyprop-2-ynyl)phenols [15–17]. In addition, some other unusual methods have been reported, such as the Wheeler aurone synthesis from chalconedihalides and a gold(I) iodide-catalyzed cyclization [18,19]. Furthermore, aurones have been obtained as byproducts in the Algar–Flynn–Oyamada synthesis of flavonols [20]. The only aurone isolated from the marine source, *Spatoglossum variable* (brownalga), was assigned the structure of 4-chloroaurone based on the interpretation of ^1H and ^{13}C NMR spectral data. The stereochemistry was assigned as *Z*, based on the calculation of heat of formations of both *Z* and *E* isomers by AM1 (the Austin model 1) method [21–23]. Stereochemistry plays a major role in the drug discovery and development; the biological activities of aurones were not studied in detail with respect to their double bond geometry (*E/Z*). Venkateswarlu et al. reported, *Z*-stereochemistry is important for the antibacterial activity [17a]. In this paper, we describe a fast and simple one-pot synthesis of new aryl-substituted aurones under room temperature conditions. We also present here the structural characterization of three 2-benzylidenebenzofuran-3-(2*H*)-one derivatives. All the compounds (**3a–c**) prepared were well characterized by spectral (IR, ^1H NMR, ^{13}C NMR, MS and HRMS) data. Thus the structures of compounds **3a–c** were examined by single crystal X-ray diffraction study which confirmed the presence of an exocyclic $\text{C}=\text{C}$ double bond with *Z*-geometry.

Experimental

General Procedures and Materials

All reactions were carried out under nitrogen atmosphere. Melting points were determined on a Büchi B-540 melting point apparatus and were uncorrected. All compounds were routinely checked by TLC and ^1H NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC, Alufolien Kieselgel 60 F254) with spots visualized by UV light. All chemicals and reagents (purity >99.8%) were purchased from Aldrich Co. Ltd., Bangalore, India.

^1H and ^{13}C NMR Spectroscopy

^1H and ^{13}C NMR spectra were determined in CDCl_3 and DMSO solutions using 400 and 100 MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0.0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (*J*) are given in Hertz.

Infrared Spectroscopy

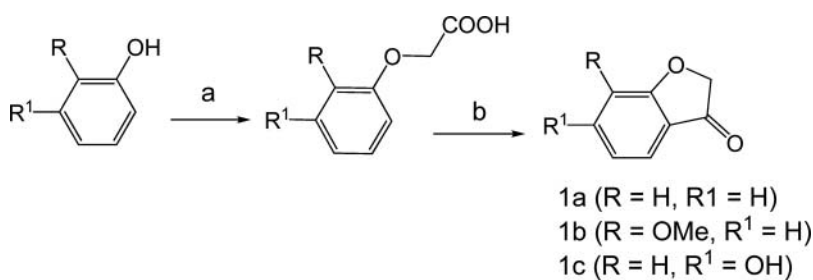
Jasco FT–IR 4200 (Easton, Maryland) type-A Fourier transform infrared spectrophotometer was used to record the IR spectra of the samples (sample concentration is 2 mg in 20 mg of KBr). The spectra were recorded over the range of $4000\text{--}600\text{ cm}^{-1}$. Data were analyzed using spectrum version 2 software (JASCO, Easton, Maryland, USA).

High Resolution Mass Spectra (HRMS)

High resolution mass spectra (HRMS) were measured on a Waters LCT Premier XE instrument (Waters Model: LCT Premier XE, Bath, United Kingdom).

Synthesis

The key starting materials, i.e., benzofuran-3(2H)-one (**1a**), 7-methoxybenzofuran-3(2H)-one (**1b**), and 6-hydroxybenzofuran-3(2H)-one (**1c**) required for our synthesis were prepared from the corresponding phenols (Scheme 1). Thus, phenol, 2-methoxy phenol and hydroxy phenol were O-alkylated with chloroacetic acid in the presence of sodium hydride to yield the desired phenoxyacetic acid intermediates, respectively, which on intramolecular Friedel-Crafts type cyclization [24a] provided the desired compounds **1a–c**. Benzaldehydes **2a–c** were prepared via alkylation, e.g., allylation and prenylation of salicylaldehyde and 5-bromo salicylaldehyde, using allyl bromide and prenyl bromide (1-bromo-3-methyl-2-butene) [24b,c].



Scheme 1. Reagents and Conditions: (a) chloroacetic acid (1.1 eq), NaH, DMF, room temp, 12 h; (b) polyphosphoric acid, 80°C, 8 h.

2-(2-(3-methylbut-2-enyloxy)benzylidene)benzofuran-3(2H)-one, (3a)

To a solution of benzofuran-3(2H)-one, **1a** (0.07 g, 0.5 mmol) in acetonitrile (5 mL) was added ethylenediamine diacetate (EDDA) (0.0094 g, 10% mol) followed by O-prenylated salicylaldehyde, **2a** (0.1 g, 0.5 mmol). The reaction mixture was stirred for 1.5 h at room temperature. The precipitate was collected by filtration and crystallized from ethanol to afford the pure compound **3a** as yellow solid (yield: 85%); mp: 89°C–91°C; ^1H NMR (400 MHz, CDCl_3): δ 8.32 (*d*, $J = 7.7$ Hz, 1H), 7.82 (*d*, $J = 7.6$ Hz, 1H), 7.64 (*t*, $J = 7.7$ Hz, 1H), 7.51 (*s*, 1H), 7.34 (*dd*, $J = 15.6, 7.2$ Hz, 2H), 7.21 (*t*, $J = 7.4$ Hz, 1H), 7.06 (*t*, $J = 7.6$ Hz, 1H), 6.93 (*d*, $J = 8.4$ Hz, 1H), 5.53 (*t*, $J = 6.3$ Hz, 1H), 4.62 (*d*, $J = 6.5$ Hz, 2H), 1.81 (*s*, 3H), 1.76 (*s*, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.7, 158.3, 155.6, 146.8, 145.9, 137.9, 132.2, 131.4, 123.6, 123.3, 121.6, 120.8, 119.5, 118.4, 115.8, 108.1, 65.5, 29.6, 25.7, 18.2; IR (KBr) ν_{max} 3032, 1698, 1647, 1297, 1242, 996, 887 cm^{-1} ; MS (ES mass): m/z 307 ($M+1$, 100%); HRMS: calcd, for $\text{C}_{20}\text{H}_{19}\text{O}_3$: 307.1324, found 307.1328.

2-(2-(allyloxy)benzylidene)-7-methoxybenzofuran-3(2H)-one, (3b)

To a solution of 7-methoxy benzofuran-3(2H)-one, **2a** (0.101 g, 0.61 mmol) in acetonitrile (5 mL) was added ethylenediamine diacetate (EDDA) (0.011 g, 10% mol) followed by O-allylated salicylaldehyde, **2b** (0.1 g, 0.61 mmol). The reaction mixture was stirred for 1.3 h at room temperature. The precipitate was collected by filtration and crystallized from ethanol to afford the pure compound, **3b** as yellow solid (yield: 92.8%); mp: 145°C–147°C;

^1H NMR (400 MHz, CDCl_3): δ 8.36 (*d*, J = 8.1 Hz, 1H), 7.54 (*s*, 1H), 7.40–7.32 (*m*, 2H), 7.17–7.06 (*m*, 3H), 6.92 (*d*, J = 8.4 Hz, 1H), 6.15–6.05 (*m*, 1H), 5.44 (*d*, J = 17.2 Hz, 1H), 5.32 (*d*, J = 10.49 Hz, 1H), 4.65 (*d*, J = 5.13 Hz, 2H), 4.03 (*s*, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.7, 157.8, 155.6, 146.9, 145.9, 132.8, 132.2, 131.3, 123.7, 123.2, 121.5, 121.1, 118.5, 117.8, 115.8, 112.0, 107.7, 69.3, 56.3; IR (KBr) ν_{max} 3055, 1697, 1649, 1277, 1239, 950, 906 cm^{-1} ; MS (ES mass): m/z 308.9 ($M+1$, 100%); HRMS: calcd, for $\text{C}_{19}\text{H}_{17}\text{O}_4$: 309.1127, found 309.1118.

2-(5-bromo-2-(3-methylbut-2-enyloxy)benzylidene)-6-hydroxybenzofuran-3(2H)-one, (3c)

To a solution of 6-hydroxy benzofuran-3(2H)-one, **1c** (0.05 g, 0.36 mmol) in acetonitrile (5 mL) was added ethylenediamine diacetate (EDDA) (0.0097 g, 10% mol) followed by 5-bromo-O-prenylated salicylaldehyde, **2c** (0.1 g, 0.36 mmol). The reaction mixture was stirred for 1.5 h at room temperature. The precipitate was collected by filtration and crystallized from ethanol to afford the pure compound, **3c** as yellow solid (yield: 89.5%); mp: 260°C–261°C; ^1H NMR (400 MHz, CDCl_3 + $\text{DMSO}-d_6$): δ 8.33 (*d*, J = 2.1 Hz, 1H), 7.63 (*d*, J = 8.4 Hz, 1H), 7.44–7.36 (*m*, 2H), 7.21 (*s*, 1H), 6.80 (*d*, J = 9.2 Hz, 1H), 6.76 (*s*, 1H), 6.71–6.69 (*m*, 1H), 5.54–5.46 (*m*, 1H), 4.58 (*d*, J = 6.54 Hz, 2H), 1.80 (*s*, 3H), 1.74 (*s*, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 181.5, 167.9, 166.6, 156.3, 147.8, 138.0, 133.1, 132.9, 125.7, 123.0, 118.9, 114.2, 113.0, 112.7, 112.6, 102.6, 98.6, 65.5, 25.5, 18.0; IR (KBr) ν_{max} 3200, 2980, 1670, 1635, 1574, 1296, 1242, 986, 897 cm^{-1} ; MS (ES mass): m/z 401 ($M+1$, 100%); HRMS: calcd, for $\text{C}_{20}\text{H}_{18}\text{BrO}_4$: 401.0388, found 401.0392.

Crystallization

The three compounds **3a–c** each 25 mg were dissolved in the ethanol in three different conical flasks and heated to aid complete dissolution. The solutions were allowed to slow evaporation and needle-shaped crystals were obtained in 1–2 days.

Preliminary Characterization

The shapes of crystals of the compounds **3a–c** were observed under the LEICA DFC295 polarizing microscope.

Single Crystal X-ray Diffraction

The single-crystal X-ray diffraction data of the crystals (**3a–c**) were collected on a Bruker Kappa APEX-II CCD DUO diffractometer at 296(2) K using graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å). No absorption correction was applied. The lattice parameters were determined from least-squares analysis, and reflection data were integrated using the program SHELXTL [25]. The crystal structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares refinement on F^2 with anisotropic displacement parameters for non-H atoms using SHELXL-97 [26]. The O–H hydrogens were located from difference Fourier maps. Aromatic and aliphatic C–H hydrogens were generated by the riding model in idealized geometries. The software used to prepare material for publication was Mercury 2.3 (Build RC4), ORTEP-3 and X-Seed

Table 1. Salient crystallographic data and structure refinement parameters of compounds **3a**, **3b** and **3c**

	3a	3b	3c
Empirical formula	C ₂₀ H ₁₈ O ₃	C ₁₉ H ₁₆ O ₄	C ₂₀ H ₁₇ BrO ₄
Formula weight	282.32	308.32	401.24
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> -1	<i>Pbcn</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>T</i> /K	296(2)	296(2)	296(2)
<i>a</i> /Å	8.4961(5)	27.9594(10)	13.2187(15)
<i>b</i> /Å	8.8991(5)	7.3164(3)	13.3753(15)
<i>c</i> /Å	11.0041(7)	15.2280(6)	20.304(2)
α /°	77.447(3)	90.00	90.00
β /°	83.382(3)	90.00	90.00
γ /°	81.717(3)	90.00	90.00
<i>Z</i>	2	8	8
<i>V</i> /Å ³	800.59(8)	3115.1(2)	3589.9(7)
<i>D</i> _{calc} /g/cm ³	1.171	1.315	1.485
<i>F</i> (000)	300	1296	1632.0
μ /mm ⁻¹	0.079	0.092	3.433
θ /°	1.90 to 27.00	1.46 to 27.00	2.39 to 18.82
Index ranges	−10 ≤ <i>h</i> ≤ 10 −11 ≤ <i>k</i> ≤ 11 −14 ≤ <i>l</i> ≤ 14	−34 ≤ <i>h</i> ≤ 34 −9 ≤ <i>k</i> ≤ 9 −19 ≤ <i>l</i> ≤ 19	−10 ≤ <i>h</i> ≤ 12 −12 ≤ <i>k</i> ≤ 10 −18 ≤ <i>l</i> ≤ 18
<i>N</i> -total	17668	35537	14081
<i>N</i> -independent	3485	3392	2973
<i>N</i> -observed	2805	2660	2392
Parameters	210	209	457
<i>R</i> _{<i>I</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0555	0.0402	0.0289
<i>wR</i> ₂ (all data)	0.1616	0.1326	0.0771
<i>GOF</i>	1.301	1.117	0.682
<i>CCDC</i>	836065	836066	836067

Table 2. Geometrical parameters of hydrogen bonds in **3a**, **3b** and **3c** compounds

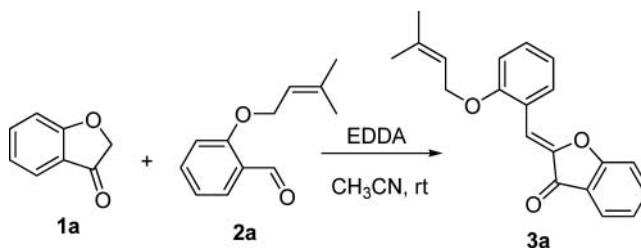
Compound	D–H...A ^a	D...A (Å)	H...A (Å)	D–H...A (°)
3a	Intra C9–H9...O3	2.7061(19)	2.34	103
	Intra C15–H15...O1	2.982(2)	2.37	123
3b	C10–H10...O4	2.7321(14)	2.35	104
	C16–H16...O1	2.9083(16)	2.26	126
3c	O3–H3...O6	2.661(6)	1.84	173
	O7–H7...O2	2.682(6)	1.86	176
	C4–H4...O7	3.269(9)	2.51	139
	C5–H5...O6	3.203(9)	2.53	130
	C15–H15...O1	2.913(7)	2.26	127
	C24–H24...O3	3.224(9)	2.42	144
	C25–H25...O2	3.224(8)	2.54	131
	C35–H35...O5	2.926(7)	2.27	127

^aAll of the C–H and O–H distances are neutron normalized to 1.083 and 0.983 Å.

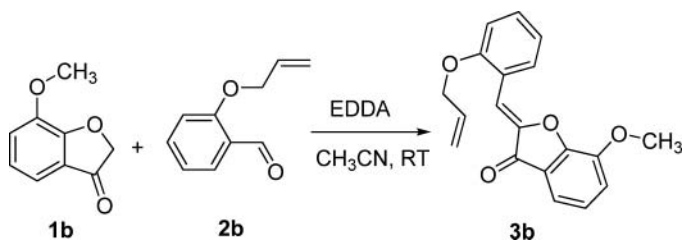
[27]. Table 1 gives the pertinent crystallographic data, and Table 2 gives hydrogen bond parameters.

Results and Discussion

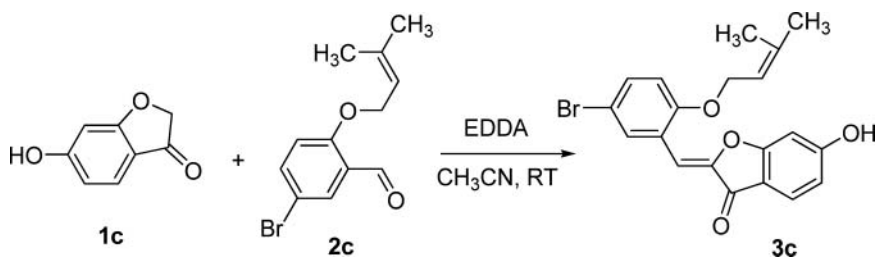
Aldol type condensation of benzofuran-3(2*H*)-one derivatives **1a–c** with suitably substituted benzaldehyde derivatives **2a–c** in the presence of ethylenediamine diacetate (EDDA) in acetonitrile provided the corresponding products **3a–c** in good yields (Schemes 2–4).



Scheme 2. Synthetic route for compound **3a**.



Scheme 3. Synthetic route for compound **3b**.



Scheme 4. Synthetic route for compound **3c**.

Infrared Spectroscopy Analysis

Infrared (IR) spectra of the compounds **3a–c** are given in supplementary material (see Figs. S1–S3). The IR spectrum of synthesized aurones (**3a–c**) showed two absorptions in the regions at 1670–1698 and 1635–1649 cm^{-1} due to the presence of α , β -unsaturated system.

NMR Spectroscopy

^1H and ^{13}C NMR spectra of the compounds **3a–c** are given in supplementary material (see Figs. S4–S9). It is known from the literature that the assignment of configuration in aurones is possible on the basis of the chemical shifts of the vinylic proton. The synthesized compounds (**3a–c**) ^1H NMR data also reveal that the vinylic proton in the structures shows siglets δ 7.51, 7.54, and 6.76 ppm, respectively. The ^{13}C NMR data also reveal that the carbonyl absorption shows region δ 184.7, 184.7, and 181.1 ppm, respectively. It is evident from the spectral data that a single geometric isomer (*Z*) was obtained in all these cases. The *Z*-isomer is known to be thermodynamically more stable than *E*-isomer and the *Z*-aurones could be photoisomerized to *E*-isomers.¹⁷ While the geometry of the double bond could be established on the basis of chemical shift value (δ) of the vinylic proton as well as carbon observed in the corresponding ^1H and ^{13}C NMR spectra [17, 28, 29], we however used X-ray single crystal study of a representative compounds to establish its molecular structure unambiguously.

High Resolution Mass Spectra (HRMS)

HRMS spectra of the compounds **3a–c** are given in supplementary material (see Fig. S10–S12) and confirm the molecular weights of the compounds.

Crystal Structure Analysis

2-(2-(3-methylbut-2-enyloxy)benzylidene)benzofuran-3(2H)-one, (**3a**). With regard to crystal structure of compound **3a**, it crystallizes in the centrosymmetric space group *P*-1 with one molecule in the asymmetric unit ($Z' = 1$) (Fig. 1). The molecular structure shows that the enyloxybenzylidene moiety is not essentially coplanar with the benzofuranone moiety (torsion angle of C1–C9–C10–C11 is 166.62°). In the crystal structure, the molecules form 1D tape-like structure. The C–H group of benzofuranone moiety of one molecule interacts with the translation-related C=O group of another benzofuranone moiety of another molecule via C–H...O hydrogen bonding and form a 1D tape-like structure along

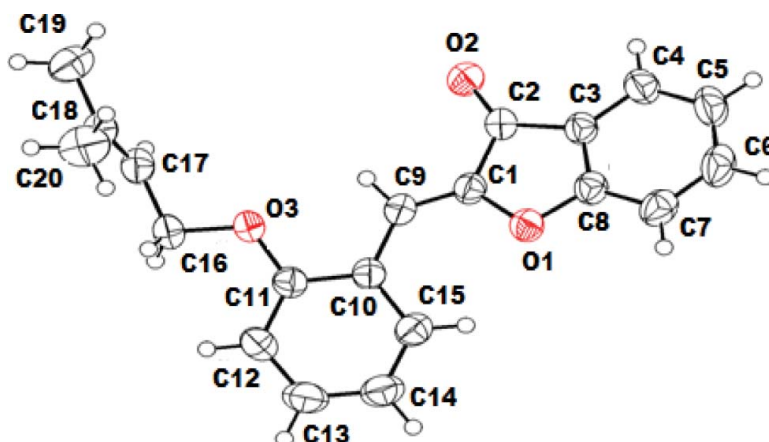


Figure 1. ORTEP representation of the compound **3a**. Thermal ellipsoids are drawn at 50% probability level.

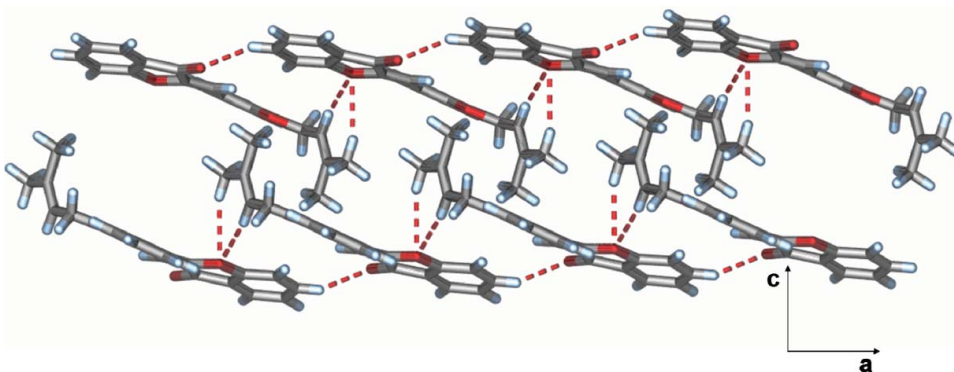


Figure 2. Packing diagram of the compound **3a**. 1D tape like structure along the crystallographic *a*-axis with C–H...O hydrogen bonding.

the crystallographic *a*-axis (Fig. 2). These 1D tapes are further stabilized by bifurcated C–H...O hydrogen bonds. The inversion-related 1D tapes are further stabilized by weak C–H... π interactions.

2-(2-(allyloxy)benzylidene)-7-methoxybenzofuran-3(2H)-one, (**3b**). The compound **3b** crystallizes in the orthorhombic *Pbcn* space group with one molecule in the asymmetric unit ($Z' = 1$) (Fig. 3). The molecular structure shows that the allyloxybenzylidene moiety is not essentially coplanar with the methoxybenzofuranone moiety (torsion angle of C1–C10–C11–C12 is 171.26°). The methoxy group on benzofuranone is coplanar with the benzofuranone moiety. The crystal structure analysis shows that the molecules form a close packed structure. The two inversion-related molecules interact via C–H...O dimer synthons and these dimers are further connected by interacting with methoxy oxygen and methoxy methyl C–H groups to form C–H...O hydrogen bonds resulting in a 1D tape-like structure (Fig. 4). These 1D tapes are further connected by several C–H...O hydrogen bonds and form a close packed structure.

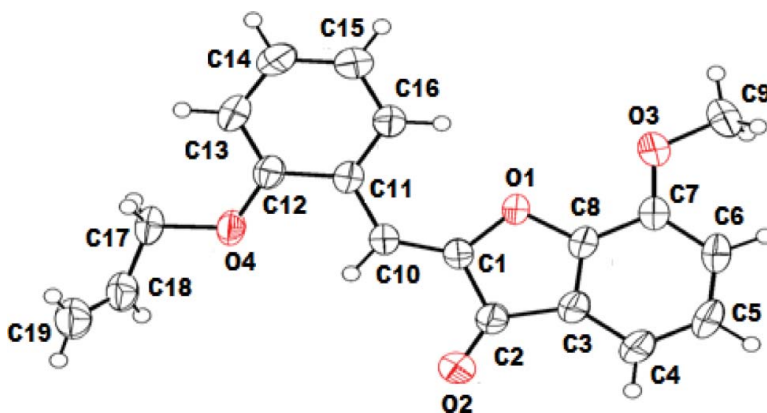


Figure 3. ORTEP representation of the compound **3b**. Thermal ellipsoids are drawn at 50% probability level.

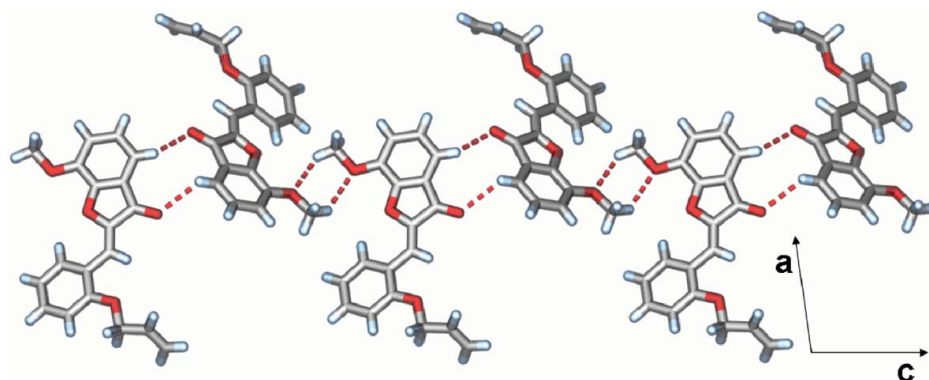


Figure 4. Packing diagram of the compound **3b**. 1D tape like structure along the crystallographic *c*-axis with C–H...O hydrogen bonding.

2-(5-Bromo-2-(3-methylbut-2-enyloxy)benzylidene)-6-hydroxybenzofuran-3(2H)-one, (**3c**). The compound **3c** crystallizes in the orthorhombic chiral $P2_12_12_1$ space group with crystallographically two symmetry independent molecules in the asymmetric unit ($Z' = 2$) (Fig. 5). The two molecules in the asymmetric unit are conformational isomers [30] and an overlay diagram of the two conformers is shown in Fig. 6. The torsion angles of 3-methylbut-2-enyloxybenzylidene (O4–C16–C17–C18 and O8–C36–C37–C38) in the two conformers are -119.37° and 124.88° . These two molecules form layered structure in the crystal. The O–H group of the hydroxybenzofuran moiety interacts with C=O group of the hydroxybenzofuranone moiety of another molecule via O–H...O hydrogen bonds to form a 1D tape-like structure along the crystallographic *a*-axis. These 1D tapes further

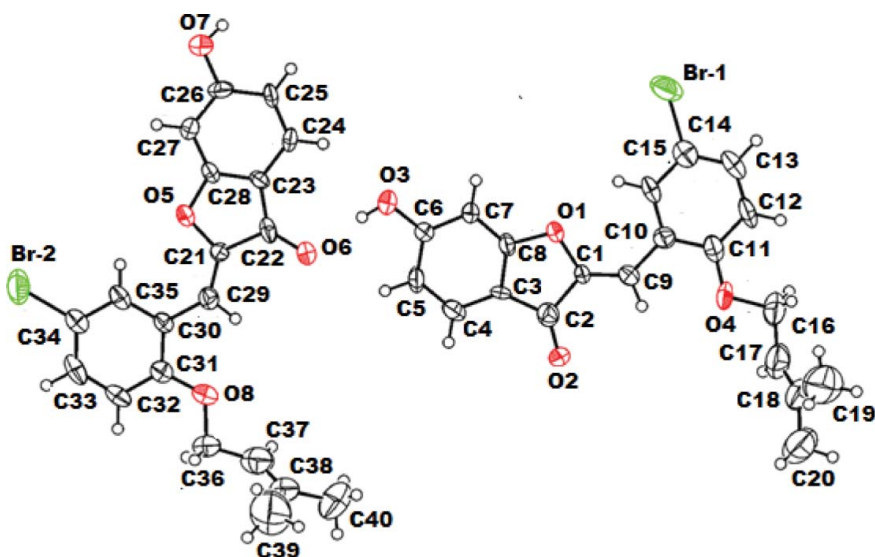


Figure 5. ORTEP representation of the compound **3c**. Thermal ellipsoids are drawn at 50% probability level.

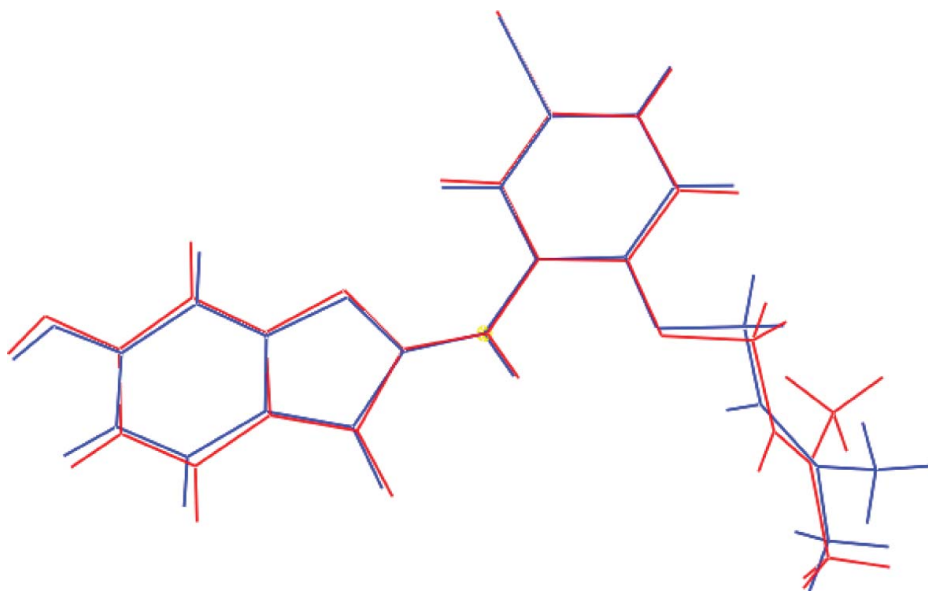


Figure 6. Overlay diagram of the two conformational isomers present in the asymmetric unit of the compound **3c**.

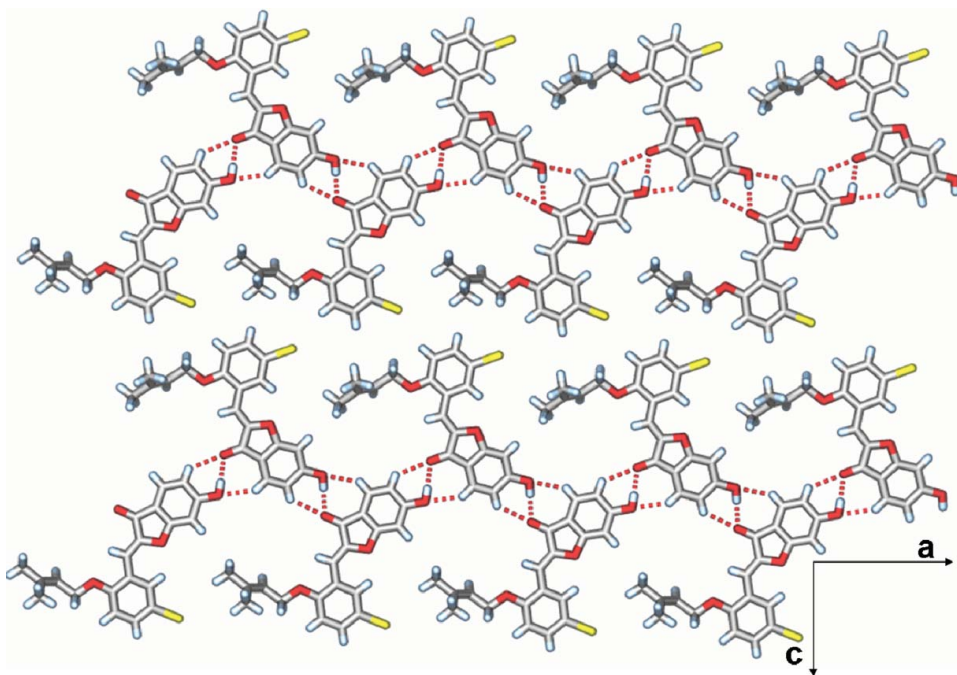


Figure 7. Packing diagram of the compound **3c**. Layered structure along the crystallographic *a*-axis with O-H...O and C-H...O hydrogen bonding.

propagate in (010) plane and form a layered structure (Fig. 7). These layers are further stabilized by C–H...O hydrogen bonds.

Conclusions

The three derivatives of 2-benzylidenebenzofuran-3-(2H)-ones were synthesized and characterized by spectral data. The structures of three compounds **3a–c** were determined by single crystal X-ray diffraction method. The geometrical configuration of all the compounds **3a–c** was confirmed as *Z*. The crystal structure analysis shows that the compounds **3a** and **3b** form 1D tapes, whereas **3c** forms a layered structure. Crystals of compound **3c** have two conformers in the asymmetric unit. The evaluation of biological activities of these compounds is in progress.

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